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COMMUNICATION

Importance of dynamic hydrogen bonds and reorientation barriers in proton transport†‡

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The dynamic nature of hydrogen bonds in phenolic polymers, where the hydrogen bond donor/acceptor reorientation can occur in a single site, presents lower barriers for proton transport.

The impact of supramolecular chemistry has been ubiquitous and clean energy technology is not an exception. We report here our new findings on designing polymers for proton transport based on the underlying supramolecular forces. Two limiting mechanisms are implicated in proton transport (PT): (i) vehicle-assisted transport, where solvent molecules (typically water) assist PT and thus the material starts losing conductivity at higher temperatures; (ii) anhydrous PT, where the conductivity typically increases with temperature, even at higher temperatures. The latter is highly sought after in proton exchange membranes (PEMs) for hydrogen fuel cells.[1] Anhydrous PT is typically considered to occur through a Grotthuss mechanism, which involves two steps (i) interfunctional group proton transfer, and (ii) regeneration of the scaffold for subsequent PT. *N*-Heterocyclic systems have been identified as promising functionalities for this non-solvent-assisted, framework conduction. Although small molecule heterocycles, for example imidazole[1a,2] and triazole,[1c] exhibit high proton conductivities in their molten states, the corresponding polymers fall far short.[1a,3] This is most likely because of the restricted mobility of the heterocycles in a tethered polymeric scaffold, which severely hinders reorientational dynamics and hence slows the overall PT rates. Note that in *N*-heterocyclic systems, one nitrogen atom accepts a proton while another nitrogen donates a proton (Fig. 1a). It is understandable that this 'two-site' feature would contribute significantly to the reorientation barrier.[4] We hypothesized that utilizing a 'single-site' moiety, which acts both as a hydrogen bond donor and acceptor, would likely provide lower reorientational barriers and thus enhanced conductivity. We report here on our initial findings on one such functional group—the phenols.

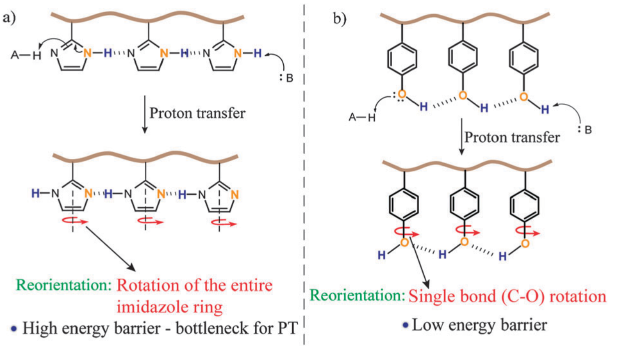

Fig. 1 Schematic representation of Grotthuss proton transfer processes in polymeric (a) imidazole; (b) phenol.

Our molecular design hypothesis is to seek a functional group that affords a dynamic and labile hydrogen bond network. This design is reminiscent of the hydrogen bond network found in water, which is interestingly one of the best Grotthuss proton transporters.[5] We hypothesized that phenols are suitable for this purpose; because they have the functional component found in water (–OH), while providing handles for polymerization. Moreover, a single hydroxyl moiety acts as both a proton acceptor and donor. Therefore, we hypothesized that phenols would exhibit lower rotational barriers (Fig. 1b). To test this hypothesis, we studied the phenolic polymers shown in Chart 1. We also carried out quantum calculations using simple model oligomers to test if (i) reorientation in phenols proceeds *via* C–O bond rotation involving just the hydroxyl moiety, and (ii) the reorientation barrier observed for the phenolic dimer is lower than that reported for *N*-heterocyclic systems,[6] and is comparable to that observed for water in nano-confined systems.[7]

We began by measuring proton conductivities of commercially available poly(4-vinyl phenol) (PS-4-OH) and the control polymers polystyrene (PS) and PS-3,4,5-triOMe, neither of which contain –OH groups. We found that PS-4-OH indeed

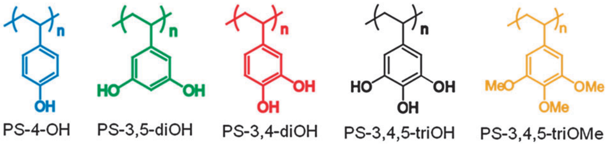

Chart 1 Structures of phenolic polymers.

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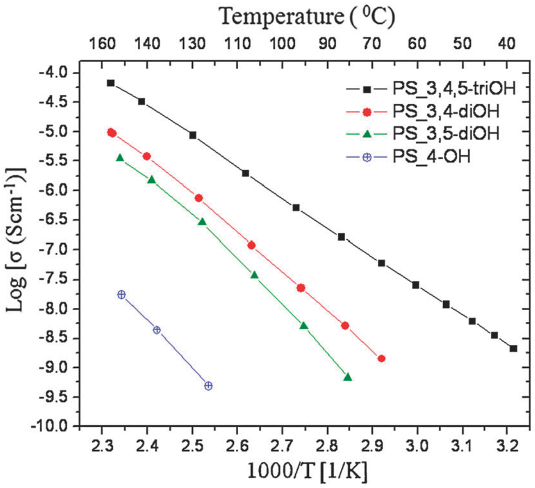

Fig. 2 Proton conductivity of phenolic polymers under vacuum.

Table 1 Proton conductivity (σ, under vacuum), apparent activation energy (E_a), glass transition temperature (T_g), and thermo-oxidative stability ($T_{d,5\%}$) of phenolic polymers

Polymer	Log [σ (S cm^{-1})] at 140 °C	E_a/kJ mol^{-1}	T_g/°C	$T_{d,5\%}{}^{a}$/°C
PS-3,4,5-triOH	−4.5	94	233	267
PS-3,4-diOH	−5.5	110	199	267
PS-3,5-diOH	−5.8	114	227	239
PS-4-OH	−8.4	154	187	285

[a] Temperature at 5% weight loss when heated under air at 1 °C min^{-1}.

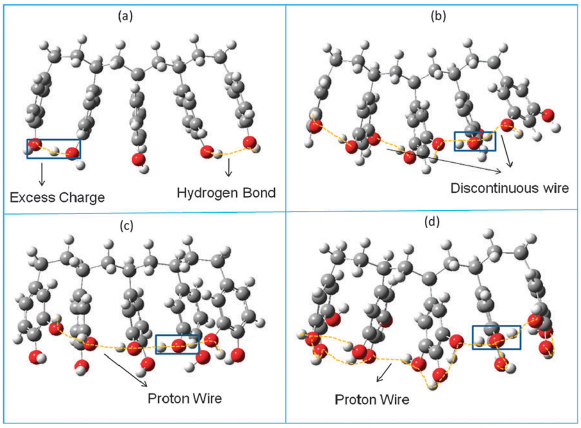

Fig. 3 Proton wires of pentamers (a) PS-4-OH; (b) PS-3,5-diOH; (c) PS-3,4-diOH; and (d) PS-3,4,5-triOH.

conducts protons under water-free conditions (σ = $10^{-7.5}$ S cm^{-1} at 160 °C) (Fig. 2). On the other hand, the proton conductivities of PS and PS-3,4,5-triOMe, neat as well as with 30% TFA doping, were below the sensitivity of the instrument ($<10^{-9}$ S cm^{-1}) over the entire temperature range. This observation is consistent with our hypothesis that –OH groups can indeed assist proton conduction even at high temperatures.

To test if regeneration involves the rotation of just C–O bonds, structures of the PS-4-OH dimer and the reoriented dimer were modeled using density functional theory (DFT) LSDA/6-311G(d,p), with transition states found using the quadratic synchronous transit method. The local spin-density approximation (LSDA) has been found to capture the energetics of π–π stacking remarkably well,[8] while most other correlation potentials miss this form of van der Waals attraction. The imaginary frequency so obtained (332*i*) corresponds to the C–O rotation of the proton around the oxygen atom.[9] The barrier for reorientation was found to be 13.7 kJ mol^{-1}, which is comparable to that observed for water in nano-confined systems (12 kJ mol^{-1}).[7] These results lend credence to our hypothesis, since C–O rotation in these phenolic species seems responsible for proton wire regeneration with barriers similar to those in water.

Although PS-4-OH can conduct protons, the observed proton conductivity is not substantial. This might be due to its inability to provide a continuous hydrogen bond pathway with just one –OH group per monomer unit, *i.e.* the fraction of conducting functionalities within the polymer may be too low. To improve the conductivity, PS-3,5-diOH, PS-3,4-diOH, and PS-3,4,5-triOH polymers (see Chart 1) were synthesized and evaluated for thermal stability (under nitrogen), thermo-oxidative stability (under air) and proton conductivity. These polymers provide a systematic variation in the number as well as the position (*ortho vs. meta*) of –OH groups and hence establish structure–property relationships. All these polymers are stable up to at least 230 °C both under nitrogen (Fig. S8, ESI‡) and air atmosphere (Table 1). Also, all these polymers exhibit enhanced proton conductivities compared to PS-4-OH (Fig. 2 and Table 1). The *ortho* (PS-3,4-diOH) *vs. meta* (PS-3,5-diOH) placement of –OH groups does not cause significant difference in proton conductivity. While the difference in conductivities between PS-3,4,5-triOH and PS-3,4-diOH is only an order of magnitude, the difference between PS-3,4-diOH and PS-4-OH is more than 3 orders of magnitude. This difference cannot simply be explained based on the number of –OH groups.

To gain insights into the observed trend in proton conductivity, hydrogen-bond networks in protonated pentamers of these polymers were investigated using DFT (LSDA/6-311G(d,p)) (Fig. 3). PS-4-OH was not found to form a continuous hydrogen bond network; instead it splits into dimers with the extra proton localized between the first dimer. For further proton translocation, the dimer between the first two units has to break and a dimer between the second and the third units must form. As such, proton translocation in PS-4-OH requires a series of hydrogen-bond breaking and forming events, which are likely limited by higher barriers. PS-3,5-diOH also does not form an extended hydrogen bond network. However, it does form localized continuous networks of a trimer and dimer. Thus, in this case, proton translocation proceeds with minimal hydrogen bond breaking and forming events compared to PS-4-OH. On the other hand, PS-3,4-diOH and PS-3,4,5-triOH form extended networks with both inter- and intra-molecular hydrogen bonds over the entire proton wire, which presumably facilitates proton translocation with lower barriers. Thus, the functional groups capable of forming both inter- and intra-molecular hydrogen bonds have greater propensities of providing continuous pathways for efficient proton shuttling across the scaffold. These same groups exhibit the highest proton conductivities, as shown in Fig. 2. The modeling studies are carried out for simple oligomers and for intrachain proton hopping. Although this provides fundamental insights into the need for multiple hydroxyl groups and thus the trends, it should be noted that they do not capture the complexities of proton transport in bulk materials, where interchain hydrogen bonds also play a key role. Also, note that the modeling efforts with oligomers do not necessarily capture the reorientational barriers associated with bulk materials. Therefore, we resorted to obtain supporting evidence for the lower reorientational barriers in phenol-based systems using experiments.

Lower T_gs are known to assist the reorientational dynamics in *N*-heterocyclic polymers due to the enhanced flexibility of the system.[3a,10] Since proton transport in *N*-heterocycles is limited by reorientation, E_a for PT has been directly correlated with T_g. If our hypothesis that phenols would exhibit low barriers for reorientation was correct, we do not expect to see a correlation between T_g and E_a in phenolic polymers. Indeed, we find that PS-3,4,5-triOH with the highest T_g has the lowest E_a of all the polymers, while PS-4-OH with the lowest T_g has the highest E_a (Table 1). In addition, the conductivity increases with the increasing number of hydroxyl groups and is not offset by the accompanying increase in T_g, which is in sharp contrast to that observed with *N*-heterocycle-based polymers.[3c] Also, the proton conductivity of the best performing PS-3,4,5-triOH polymer compares very well with the molten state conductivities of the corresponding small molecule, pyrogallol (Fig. S9, ESI‡). In contrast, the proton conductivities observed in imidazole based polymeric systems are at least two orders of magnitude lower than the molten state conductivity of imidazole, which is attributed to be arising from the restricted reorientational dynamics with immobilization.[1a] Thus, considering the inverse correlation between T_g and E_a and the comparable conductivities of PS-3,4,5-triOH and pyrogallol, it is reasonable to suggest that the PT in phenols is not limited by reorientation.

Finally, we also envisaged the possibility that conductivities would be enhanced with humidity, as water would add to the available pathways for proton transduction at lower temperatures. To test this, we exposed the polymer films to 30% relative humidity and measured the conductivities under those conditions. Indeed, the proton conductivities of the phenolic polymers were enhanced by about two orders of magnitude, especially in the lower temperature regime as anticipated (Fig. S10, ESI‡).

From a practical materials perspective, we recognize that the proton conductivities of these polymers are lower than Nafion.[12a] Also, chemical stability may be an issue with phenols due to the possibility of conversion to quinones. Such concerns are partly offset by the fact that these polymers exhibit excellent thermo-oxidative stabilities in air, as ascertained by TGA. Most importantly, this work provides a critical fundamental insight using phenols as the test case—PT moieties with a 'single-site' hydrogen bond donor/acceptor capabilities can lead to reduced reorientation energies, which impacts PT efficiencies.

In summary, we have demonstrated that (i) phenolic systems can conduct protons under anhydrous conditions by forming a dynamic hydrogen bond network, akin to that observed in water; (ii) proton wire in phenolics can be regenerated simply by rotating about the C–O bond; and (iii) proton transport in phenolic polymers is most likely not limited by reorientation. Perhaps, the most important conclusion is that while the classical search for functional groups involved acidic ($–SO_3H$, $–H_2PO_3$)[11,12] or basic functional groups (imidazoles, triazoles)[1] to conduct protons, it is equally (if not more) important to consider dynamic hydrogen bonding systems for PT. In other words, reorientation should be considered as a crucial design parameter for protogenic groups in PT. Although other systems (*e.g.* phosphonic acid)[12] can be envisioned to require minimal reorientation, the PT in these materials has not yet been examined in that context. Thus, we believe that our findings pave the way for the design of new protogenic groups with minimum reorientation barrier for efficient proton transport. This design principle, in concert with nanostructuring strategies,[1e,13] will likely lead to proton transport materials with markedly advanced performance.

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